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# III.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

## RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

BY C. LORING JACKSON AND ALFRED W. FIELD.

### FOURTH PAPER.

### PARACHLORBENZYL COMPOUNDS.

Presented December 12th, 1877.

*Parachlorbenzylchloride*, $C_6H_4ClCH_2Cl$. In beginning these researches, we had no idea that it would be necessary to investigate this substance, as, since its discovery by Beilstein and Geitner,* it had been prepared and studied by a great number of chemists, and had served as the starting-point for the preparation of all the parachlorbenzyl compounds known. But, on looking into the subject more carefully, we found that it had been made invariably from the product of the chloriring of toluol in the cold, which Hübner and Majert † have proved, by their work on the sulpho-acids, is a mixture of ortho and parachlortoluol; while, more recently, Oscar Emmerling ‡ has shown that the product from oxidizing it with potassic permanganate contains more ortho than parachlorbenzoic acid. The parachlorbenzylchloride of previous chemists, therefore, must have been contaminated with a larger or smaller amount of the ortho compound, which escaped detection, because the method used by them to test the purity of their preparations consisted in oxidizing with potassic dichromate and sulphuric acid, and, as this destroys the ortho modification completely, a pure parachlorbenzoic acid was the only product. This oversight is not surprising when it is borne in mind that the more important of

* Beilstein and Geitner, Zeitschr. der Chem., 1866, p. 307; also p. 17.
† Hübner and Majert, Ber. D. Ch. G. vi. p. 790.
‡ O. Emmerling, Ber. D. Ch. G. viii. p. 880.

these papers appeared in 1866, when the nature of aromatic isomeres was very imperfectly understood.

For the reason given above, we determined to prepare the parachlorbenzylchloride from perfectly pure parachlortoluol, and hoped that it might be a solid, instead of the oily liquid described by our predecessors; indeed, it seemed hard to believe that it could be a liquid, as the parachlortoluol melts at 6½° (Hübner and Majert), and we had already found that the introduction of bromine into the side-chain raised the melting-point to 48½°.

*Preparation.* Parachlortoluol was made from pure paratoluidine by treatment with hydrochloric acid and potassic nitrite, according to a modification of the method of Hübner and Majert,* described in connection with parachlorbenzylbromide in the first paper † of this series. The 31 grs. that we obtained distilled over completely between 160° and 161°, and froze between 4° and 5° in white plates looking exactly like parabromtoluol, which melted from 7° to 7½°. These results agree essentially with those of Hübner and Majert,* who found the boiling-point 160½°, the freezing-point a little above 0°, and the melting-point 6½°. To convert this into parachlorbenzylchloride, a stream of chlorine was passed into it while it stood in a paraffine-bath heated to 166°: when the increase in weight showed that somewhat more than the calculated amount of chlorine had been taken up (the 27 grs. of parachlortoluol used had become 35 grs. instead of 34.3 grs.), the chlorine was stopped, and the product put in a freezing mixture of ice and salt, where it partially solidified in white needles, which were drained on the filter-pump, and recrystallized from alcohol. The yield was very small, and all attempts to get more from the mother-liquors were fruitless. The following analyses of the substance dried *in vacuo* show that it is the expected parachlorbenzylchloride.

0.6760 gr. of substance gave 1.2930 gr. of $CO_2$ and 0.2458 gr. of $H_2O$.‡

0.2755 of substance gave, by Klobukowski's § modification of Emil Kopp's method, 0.4946 gr. AgCl.

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* Hübner and Majert, Ber. D. Ch. G. vi. p. 794.

† These Proceedings, XII. (N. S. IV.) p. 218.

‡ Combustion of these parachlorbenzyl compounds with plumbic chromate alone was found to yield good results much more easily than the more usual method of combustion in a stream of oxygen, and therefore was used in the analysis of all these substances.

§ Klobukowski, Ber. Dt. C. G. 10, p. 290.

| | Calculated for $C_7H_6Cl_2$. | Found. |
|---|---|---|
| Carbon | 52.17 | 52.17 |
| Hydrogen | 3.73 | 4.04 |
| Chlorine | 44.10 | 44.41 |
| | 100.00 | 100.62 |

*Properties.* White lustrous prisms or needles, often more than 3 cm. long, with an agreeable aromatic odor and most violent action on the mucous membrane and tenderer parts of the skin; melting-point, 29°; so volatile that a crystal exposed to the air disappears in a few hours; sublimes even at ordinary temperatures in needles; it is very little, if at all, soluble in water, but readily in warm, less so in cold, alcohol, very easily in ether, benzole, carbonic disulphide, and glacial acetic acid. That it is a chlorbenzyl compound was proved by boiling it for some time with water, in a flask with a return-cooler, when the parachlorbenzylalcohol and hydrochloric acid were formed. Boiled with a solution of potassic permanganate, it was easily oxidized, giving an acid which melts between 233° and 235° (O. Emmerling gives 234° as the melting-point of parachlorbenzoic acid); this acid boiled with water, in which the orthochlorbenzoic acid is much more soluble than the para, gave a solution which deposited crystals melting also at 233°–235°: as potassic permanganate oxidizes instead of destroying the ortho compounds, this proves that our parachlorbenzylchloride is perfectly free from isomeric impurities.

Having thus proved that the parachlorbenzylchloride used as a starting-point for the preparation of derivatives by Beilstein, Kuhlberg, Neuhof, and others, really did contain the ortho compound, as we had previously inferred, we next proceeded to make some of these derivatives, and redetermine their properties. In this work, the more easily purified parachlorbenzylbromide was used instead of the chloride.

*Parachlorbenzylalcohol,* $C_6H_4ClCH_2OH$, was made by boiling the bromide (or chloride) with water in a flask with a return-cooler. The formation of hydrobromic (or hydrochloric) acid by this reaction was proved by testing the water, which had become acid, with argentic oxide, when argentic bromide (or chloride) was formed, and the acid reaction disappeared. The alcohol was made also from the acetate by boiling with water: sealing with aqueous ammonia, as recommended by Beilstein and Kuhlberg, being found in this case unnecessary: it was purified by crystallization from boiling water, dried *in vacuo*, and analyzed.

0.4517 gr. of substance gave 0.9754 gr. $CO_2$ and 0.2175 gr. $H_2O$.

| | Calculated for $C_7H_6ClOH$. | Found. |
|---|---|---|
| Carbon | 58.94 | 58.89 |
| Hydrogen | 4.91 | 5.34 |

*Properties.* Beautiful pointed white ribbons usually one or two inches long, with a brilliant pearly lustre and characteristic smell, but no action on the mucous membrane or tenderer parts of the skin; melting-point, 70½° ; sublimes very easily in white needles, and can be purified in this way; evaporates slowly on exposure to the air, and distils in a current of steam; slightly soluble in cold, much more so in hot water, very easily in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid. It is oxidized by a mixture of potassic dichromate and dilute sulphuric acid, giving parachlorbenzoic acid ; melting-point, 233° (234° O. Emmerling).

The chlorbenzylalcohol obtained by Beilstein and Kuhlberg * differs from the above only in melting at 66°.

*Parachlorbenzylcyanide.* The product of the reaction of alcoholic parachlorbenzylbromide and potassic cyanide, when precipitated by water, was a yellow oil, which showed no signs of solidifying in a mixture of ice and salt: after standing in an open watch-glass for three or more weeks, however, it did deposit crystals when put in a freezing-mixture, but in such small quantity that it was impossible to purify them thoroughly; and it did not seem worth while to spend the large amount of time and material necessary to get enough of them for complete study. The crystals, after sucking out the oil with filter-paper, proved to be good-sized colorless prisms; and, as one specimen of a twinned form like a quatrefoil was observed, there can be no doubt that the substance is analogous to the parabrombenzylcyanide: † its melting point is 29° ; and it is easily soluble in alcohol and ether, being left on evaporation of the solvent as an oil which crystallizes when stirred.

The yellow oil from which the crystals were obtained has also the nitrile smell, and is converted, by heating to 100° in a sealed tube with hydrochloric acid, into parachloralphatoluylic acid: it must therefore be either the same substance as the crystals, prevented from solidifying by a small quantity of impurity, or the crystals may be a polymeric form of the oil. The cyanide was mentioned by Neuhof ‡

* Beilstein and Kuhlberg, Ann. Chem. Pharm. 147, p. 339.

† These Proceedings, XII. (N. S. IV.) p. 222.

‡ Neuhof, Ann. Chem. Pharm. 147, p. 347.

as a dark oil, made by heating chlorbenzylchloride to 120°–130° in a sealed tube with potassic cyanide and alcohol; but no attempt was made to purify or analyze it. This heating in a sealed tube to 120°–130° is, as seen from the above, unnecessary.

*Parachloralphatoluylic Acid,* $C_6H_4ClCH_2COOH$, made by heating the nitrile to 100° in a sealed tube with fuming hydrochloric acid, or by boiling it with dilute sulphuric acid in a flask with a return-cooler, was purified by solution in ammonic hydrate, precipitation with sulphuric acid, and recrystallizing from boiling water. Its composition was established by an analysis of the silver salt.

*Properties.* White needles, often two centimetres long, sometimes thick and pointed, with a pleasant smell; melting-point, 103½°–104°; sublimes easily in little plates, and can be distilled, although not quickly, in a current of steam; somewhat soluble in cold, much more so in hot water, freely in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid. Aqueous ammonia dissolves it readily, but the ammonic salt is decomposed, at least in part, by evaporation the acid being set free.

A chloralphatoluylic acid has been already described as the para compound by Neuhof,* who made it, however, from chlorbenzylchloride; the melting-point was 60°, and it separated from its salts as an oil which soon solidified, otherwise it resembled our acid, except that it seems to have been much more soluble in water. Later, Radziszewski † made a similar acid, melting at 68° by chloriring alphatoluylic acid.

*Argentic Parachloralphatoluylate,* $C_6H_4ClCH_2COOAg$, fell as a white, curdy precipitate, upon adding argentic nitrate to a neutral solution of the ammonic salt of the acid. It was washed with water, dried at 100°, and analyzed.

0.3410 gr. of substance gave, precipitated from a nitric acid solution, with hydrochloric acid, 0.1788 gr. of AgCl.

| | Calculated for $C_8H_6ClO_2Ag$. | Found. |
|---|---|---|
| Silver | 38.91 | 39.44 |

*Properties.* A white, curdy mass, consisting of clumps of silky microscopic needles, which blackens rapidly in direct sunlight, but only very slowly in diffused daylight; very slightly soluble in boiling water, almost insoluble in cold, freely soluble in dilute nitric acid and ammonic hydrate.

* Neuhof, Ann. Chem. Pharm. 147, p. 347.
† Radziszewski, Ber. D. Ch. G. ii. p. 207.

Neuhof obtained a similar salt, but describes it as more soluble in water than ours.

We did not succeed in getting a pure, well-defined *calcic salt*, although we tried to do so several times. By adding lime-water to the acid till the reaction was alkaline, removing the excess of lime by carbonic dioxide, and allowing the solution to evaporate spontaneously, arborescent groups of white needles were obtained. These lost 9.84 per cent when dried at 100°; 2 molecules of crystal water would give 8.68 per cent; $2\frac{1}{2}$ molecules, 10.61 per cent; the loss, therefore, does not correspond to any probable amount of water of crystallization, and it seemed likely that something beside water was given off, as there was a slight sublimate on the upper watch-glass, and the substance had become somewhat brown, with a semifused look very unlike its original appearance. It, however, contained 10.36 per cent of calcium, and may therefore have been the anhydrous salt which needs 10.55 per cent. Other experiments under different conditions gave no better results, and we therefore decided that the salt was not important enough to repay a thorough study, which would use up a great deal of time.

The *baric salt* was even less well defined than the calcic: it was prepared in the same way, and appeared on evaporation of its solution over sulphuric acid as a colorless varnish, part of which changed on stirring into a radiated crystalline mass. This became white and opaque when treated with cold water, and when boiled with water gave an acid reaction and the smell of the acid. If the solution was evaporated on the water-bath instead of over sulphuric acid, a sticky gum was left. Neuhof's baric salt was similar to ours, and gave him an amount of barium corresponding to an acid salt. His calcic salt, on the other hand, contained one molecule of water, which it lost at 100°.

A solution of the acid in ammonic hydrate, from which the excess of ammonia has been driven off on the water-bath, gives reactions with salts of the various metals similar to those of the corresponding brom-acid.* The bluish-green flocks with *cupric sulphate*, yellowish-brown with *ferric chloride*, and white with *plumbic acetate* or *mercurous nitrate* are especially characteristic.

*Parachlorbenzylsulphocyanate*, $C_6H_4Cl\,CH_2SCN$, made by boiling the bromide with an alcoholic solution of potassic sulphocyanate, was purified by freezing with snow and salt, sucking out the oil with filter-

* These Proceedings, XII. (N. S. IV.) p. 225.

paper, and recrystallization from alcohol with the help of a freezing-mixture. It was dried *in vacuo* and analyzed.

0.1569 grs. substance gave 0.1985 grs. $BaSO_4$.

| | Calculated for $C_7H_6ClSCN$. | Found. |
|---|---|---|
| Sulphur | 17.43 | 17.38 |

*Properties.* White, flattened needles, often over an inch long, with a strong, disagreeable smell; melting-point, 17°; does not distil with steam, but seems to be slowly decomposed by it, a few brown drops with a smell like that of benzaldehyd passing over; mixes with alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid, but not with water.

This substance has not been made heretofore: it resembles the corresponding bromine compound very closely in every thing but melting-point.

### Parachlorbenzylamines.

These substances have been studied already by Berlin,* who prepared them by heating the chlorbenzylchloride with alcoholic ammonia for one week in the steam-bath. The product was worked up by a needlessly complex process, consisting, when stripped of its unnecessary steps, in separating one portion of the bases by conversion into their chlorides and crystallizing from alcohol, while in the remainder the tertiary amine was destroyed by distillation with bromine and water, and the bromides of the remaining amines separated by crystallization. The properties of the tertiary and primary amines, as described by him, are in no way peculiar; but he obtained four isomeric forms of the secondary amine, which were themselves undistinguishable yellow oils, but differed in the melting-points of their salts, as shown in the following table: —

| Name of Salt. | Melting Points. | | | |
|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ |
| Chloride . . . . | 288°–289° | 225°–228° | 218°–220° | 221°–222° |
| Bromide . . . . | 283°–290° | 224° | 210°–212° | 198°–199° |
| Iodide . . . . | . . . . | 215° | 187° | 216°–218° |
| Nitrate . . . . | . . . . | 204°–205° | 193° | 177°–179° |

These salts also differed in solubility, the $\alpha$ modification being the least, the $\delta$ the most soluble: they were separated by crystallization

* Berlin, Ann. Chem. Pharm. 151, p. 137.

of the bromides from water. These observations rendered a repetition of Berlin's work very interesting; but we did not follow the process given by him, as we have found a much more easy and simple method for the separation of the bases. Alcoholic ammonia acted very quickly, even in the cold, on parachlorbenzylbromide: the product from this or from the action in a sealed tube at 100° consisted of crystals either of the bromide of the tertiary amine or of the base itself, and of an alcoholic solution, which, filtered off and evaporated on the steam-bath, yielded the bromides of ammonium and of the primary and secondary amines with some free tertiary amine. This residue, after washing with water to remove the bromides of ammonium and the primary amine, was repeatedly crystallized from hot alcohol, until it was divided into slightly soluble scales of secondary bromide and needles of the free tertiary amine readily soluble in boiling alcohol.

*Triparachlorbenzylamine*, $(C_6H_4ClCH_2)_3N$, was freed from a trace of bromide by crystallizing from ether, dried *in vacuo*, and analyzed.

0.7096 grs. of substance gave 1.6780 grs. $CO_2$, and 0.3300 grs. $H_2O$.

| | Calculated for $(C_7H_6Cl)_3N$. | Found. |
|---|---|---|
| Carbon | 64.78 | 64.49 |
| Hydrogen | 4.61 | 5.16 |

*Properties*. Bunches of white needles, when crystallized from alcohol; from ether it separates as an oil, which solidifies after some time in flattened prisms; it is also deposited from the action of cold alcoholic ammonia on parachlorbenzylbromide in short, thick, well-formed crystals, with rhombic faces; melting-point, 78½°; insoluble in water, very slightly soluble in cold, freely in hot alcohol, and in ether, benzole, and carbonic disulphide, less so in glacial acetic acid.

The *chloride* was obtained in an impure state when an alcoholic solution of the base was heated with strong hydrochloric acid; after standing 24 hours, the solution was allowed to evaporate spontaneously, when balls of radiated needles were left which melted at about 196°, were soluble in alcohol, ether, and glacial acetic acid, slightly in water, and insoluble, or nearly so, in carbonic disulphide and benzole; the alcoholic solution left a viscous mass, which changed into needles slowly. After drying *in vacuo*, it lost, in the steam-bath, an amount equal to less than one molecule of water; but its melting-point was unaltered, and, as it yielded crystals of the free amine on repeated treatment with alcohol, it does not follow that the loss was nothing but water. We could find no satisfactory method of purifying this, or of making a purer substance. The *bromide* obtained in the prepa-

ration of the amines crystallizes in scales like those of the bromide of the secondary amine soon to be described, but less soluble in alcohol.

*Triparachlorbenzylamine Chlorplatinate*, $[(C_6H_4ClCH_2)_3NH]_2PtCl_6$, was made by adding aqueous platinic chloride to an ethereal solution of the base, and washing with water, alcohol, and ether; dried at 100°, it gave the following results on analysis: —

I. 0.2380 grs. substance gave 0.0405 grs. platinum.
II. 0.2796 grs. substance gave 0.0471 grs. platinum.

| | | Found. | |
|---|---|---|---|
| Calculated for $[(C_7H_6Cl)_3NH]_2PtCl_6$. | | I. | II. |
| Platinum | 16.54 | 17.01 | 16.84 |

*Properties.* Pale orange microscopic irregular plates, almost insoluble in water, alcohol, and ether.

It is worthy of especial note that Berlin's tertiary chlorbenzylamine melted at 88°–89°, as this is the only case in which we have found the melting-point of the pure substance lower than that of the impure. His chloride melting-point, 170°–175°, crystallized in well-formed rhombohedra with two molecules of water, which it lost *in vacuo*. Our (impure) salt differed from his not only in appearance and melting-point, but also in losing nothing *in vacuo;* and we have never observed any rhombohedra like those described by him, although we have tried very often and under various conditions to obtain them.

*Diparachlorbenzylamine*, $(C_6H_4ClCH_2)_2NH$. The bromide of this base, separated from the other amines as described above, and purified by repeated boiling with alcohol, was decomposed with aqueous sodic hydrate; the oil thus obtained solidified on stirring, especially if it was touched with a crystal of the substance.

*Properties.* White radiating bladed crystals; melting-point, 29°; insoluble in water, soluble in alcohol and glacial acetic acid, freely soluble in ether, benzole, and carbonic disulphide.

The *chloride* fell as a white precipitate on adding hydrochloric acid to an alcoholic solution of the base; microscopic rhombic and prismatic plates apparently monoclinic, slightly soluble in water, alcohol, and glacial acetic acid, insoluble in ether and carbonic disulphide; melting-point, 288°.

*Diparachlorbenzylamine Chlorplatinate*, $[(C_6H_4ClCH_2)_2NH_2]_2PtCl_6$, made by adding aqueous platinic chloride to the alcoholic solution of the base, and purified by washing with water, was dried at 100°, and analyzed.

0.2389 grs. substance gave 0.0496 grs. platinum.

| | Calculated for $[(C_7H_6Cl)_2NH_2]_2PtCl_6$. | Found. |
|---|---|---|
| Platinum | 20.90 | 20.76 |

*Properties.* Pale yellow scales (deeper in color than the corresponding salt of the tertiary amine), slightly soluble in boiling water, almost insoluble in cold water and alcohol.

The *bromide* of the base was obtained during the preparation of the amines in white scales very slightly soluble in water or alcohol, insoluble in ether, easily decomposed by aqueous sodic hydrate, and melting with decomposition between 280° and 290°.

The salts just described are identical with those of the $\alpha$ modification of Berlin's secondary chlorbenzylamine; and, as we could find no trace of any other modifications, there can be but little doubt that the $\beta$, $\gamma$, and $\delta$ forms of Berlin consisted of mixtures of para- and ortho-compounds, in varying proportions, and this view is still further supported by the fact that the melting-points of these so-called isomeres are very near together, those of the chlorides in fact all lying within ten degrees.

*Monoparachlorbenzylamine*, $C_6H_4ClCH_2NH_2$, precipitated from the aqueous solution of its bromide with sodic hydrate and distilled with steam forms a colorless oil nearly, if not completely, insoluble in water, but soluble in ether; on exposure to the air it is converted, almost at once, into a white soluble crystalline carbonate; if therefore care is not taken to exclude carbonic anhydride, small quantities of the amine seem to dissolve easily in water.

The *carbonate* was made by exposing the free base to carbonic anhydride or even to the air, and was always left when an ether extract containing the base was allowed to evaporate spontaneously. Crystallized from water, it forms white plates often of considerable size, from alcohol needles; melting-point, 114°–115°; it dissolves slowly in cold, quickly and freely in hot water and alcohol; sodic hydrate sets free the oily amine.

The *chloride* made by dissolving the carbonate in hydrochloric acid crystallizes in long, narrow white plates, soluble in water and alcohol, sparingly soluble in glacial acetic acid, and essentially insoluble in ether, benzole, and carbonic disulphide; melting-point, 239°–241°.

*Monoparachlorbenzylamine Chlorplatinate*, $(C_6H_4ClCH_2NH_3)_2PtCl_6$, made by mixing a solution of the chloride of the base with platinic chloride, purified by washing with a mixture of alcohol and ether, and dried at 100°, gave the following result:—

0.3067 grs. substance gave 0.0866 grs. platinum.

| | Calculated for $(C_7H_6ClNH_3)_2PtCl_6$. | Found. |
|---|---|---|
| Platinum | 28.39 | 28.23 |

*Properties.* Bright yellow branching plates or needles, arranged in round woolly groups when crystallized from water, in which and alcohol it is decidedly soluble.

The *bromide* of the base formed in the preparation of the amines resembles the chloride in appearance and solubility, but is somewhat less soluble in cold water, and melts with decomposition between 225° and 230°.

The foregoing results differ from those obtained by Berlin only in the melting-point of the chloride, which he found 197°; he gives no melting-points for the carbonate and bromide.

To make it easier to compare the new melting-points with those in use heretofore, we have collected them in the following table; the second column of which gives the melting-points of the pure substances made by us, and the third the melting-points determined by the chemists mentioned in the fourth column.

| Name of Substance. | True Melting-point | Old Melting-point | Authority for Old Melting-point. |
|---|---|---|---|
| Parachlorbenzylchloride . . . | 29° | Liquid. | Beilstein and Geitner. |
| Parachlorbenzylbromide . . . | 48½° | | |
| Parachlorbenzylalcohol . . . | 70½° | 66° | Beilstein and Kuhlberg. |
| Parachlorbenzylcyanide . . . | 29° (?) | Liquid. | Neuhof. |
| Parachloralphatoluylic Acid . | 103½–104° | 60° | Neuhof. |
| | | 68° | Radziszewski. |
| Parachlorbenzylsulphocyanate | 17° | | |
| Primary Amine . . . . . . . | Liquid. | Liquid. | Berlin. |
| " " Chloride . . . | 239°–241° | 197° | " |
| " " Bromide . . . | 225°–230° | | |
| " " Carbonate . . | 114°–115° | | |
| Secondary Amine. . . . . . . | 29° | Liquid. | Berlin. |
| " " Chloride . . | 288° | 288°–289° | " |
| " " Bromide . . | 280°–290° | 283°–290° | " |
| Tertiary Amine . . . . . . . | 78½° | 88°–89° | " |
| " " Chloride . . . | 196° (?) | 170°–175° | " |

The revision of the parachlorbenzyl compounds will be continued in this laboratory; in fact, the aldehyde and some of the sulpho-derivatives have been already made and partially studied by Mr. J. Fleming White, whose work will form the subject of a later paper of this series.